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Energetic, Low Melting Salts of Simple Heterocycles

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SUMMARY

The synthesis of three new families of heterocyclic based salts was undertaken and accomplished. Three triazole systems, 1-H-1, 2, 4-triazole 4-amino-1, 2, 4-triazole, and 1-H-1, 2, 3-triazole were used as proton bases with nitric (HNO_3), perchloric (HClO_4), and dinitramidic (" $\text{HN}(\text{NO}_2)_2$ ") acid systems. In all cases, stable salts were recovered and fully characterized by vibrational spectra (IR, Raman), multinuclear nmr spectroscopy, material balance, density measures, elemental analyses, as well as DSC, TGA and initial safety testing (impact). Many of these salts have melting points well below 100°C , yet high decomposition onsets, defining them as new, highly energetic members of the well known class of materials identified as ionic liquids.

INTRODUCTION

The Air Force continues a quest for new energetic materials as part of its basic and applied research program. The general requirements for the molecules include, (1) High density and energy; (2) Thermal/Storage stability; (3) Low handling hazards (e.g., low sensitivity to impact, friction, electrostatic discharge, and low toxicity.); and (4) Simple production routes (i.e., three or less synthesis steps) for low cost. In our laboratory, we have been pursuing the synthesis of new energetic salts. Energetic materials that are salt-based often possess advantages over nonionic molecules. First, salts tend to have very low vapor pressure, which essentially eliminates the risk of exposure of personnel to new materials via a major exposure route (inhalation). Second, ionic compounds often have higher density than atomically similar, nonionic molecules.

This can generally be attributed to the influence of coulombic forces to form ordered and dense lattice structures in molecular assemblies.

The triazoles, 1H-1,2,4-triazole, 4-amino-1,2,4-triazole, and 1-H-1,2,3-triazole have high calculated heats of formation of +47 kcal/mole, +76 kcal/mole, and +65 kcal/mole respectively¹⁻³, are commercially available, and were chosen to make new families of energetic salts. (Figure 1) Except for one Russian report on a complex between 4-amino-1,2,4-triazole and trinitromethane⁴, energetic salts of these heterocycles have not been disclosed.

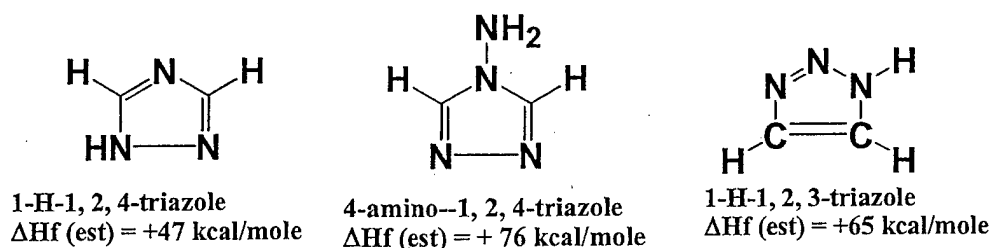


Figure 1. The heterocycle systems under study.

Salts consisting of the protonated heterocycle paired with either the nitrate, perchlorate, or dinitramide anion were synthesized in high yield and purities, characterized by vibrational spectra, multinuclear nmr, differential scanning calorimetry, and elemental analyses. These two new families of salts have good heats of formation, high densities, and favorable oxygen balances for self combustion.

EXPERIMENTAL

Caution! Despite the fact that no mishaps were encountered with any of these new salts, proper safety equipments (face shield, leather gloves, blast shields) should be used in synthesizing and handling all of these materials, most notable being the highly impact sensitive 4-amino-1,2,4-triazolium dintramide and 1-H-1,2,3-triazolium perchlorate. 1-H-1,2,4-triazole, 4-amino-1,2,4-triazole, and 1-H-1,2,3-triazole were purchased from Aldrich Chemical Company, and after ¹H and ¹³C studies revealed no impurities, they were used as received. Nitric acid, HNO₃ (69-70% by weight; H₂O solution; A.C.S. reagent grade) was purchased from Aldrich Chemical Company, and used without further purification. Perchloric acid, HClO₄ (70.0% by weight, H₂O solution; Baker Reagent

grade) was used as received. Ammonium dinitramide, $\text{NH}_4\text{N}(\text{NO}_2)_2$, was graciously donated from ATKThiokol, Inc., and after Raman spectroscopy showed low NO_3^- content, it was stored in a brown bottle inside a nitrogen filled glove box. Methanol, CH_3OH , HPLC grade Aldrich, was dried over sodium metal and subsequently distilled. Ether, anhydrous, 99.5% Aldrich, was dried with activated alumina prior to its use. Ethyl acetate, 99.8%, HPLC grade anhydrous, was dried over magnesium sulfate and distilled prior to use. All solvents were stored inside glass vessels, which were sealed with teflon screw-cap plugs, and were equipped with #15 O-ring fittings. Infrared spectra were recorded as KBr disks (using a KBr disk as a reference background) on a Nicolet 55XC FT-IR spectrometer from 4000-400 cm^{-1} . Raman spectra were recorded in pyrex melting point capillaries on Bruker Model FRA 106/S Equinox 55 Raman spectrometer equipped with a 1.06 micron IR excitation laser. NMR experiments were carried out by dissolving the salts in CD_3OD in 5mm nmr tubes, and the ^1H and ^{13}C spectra recorded on a Bruker Spectrospin DRX 400 MHz UltrashieldTM NMR. Thermal analyses were carried out in hermetically sealed, coated aluminum pans on a Thermal Analyst 200, Dupont Instruments 910 Differential Scanning Calorimeter. Samples were prepared and sealed inside a nitrogen-filled glove box, and once the pans were inside the DSC cell, the cell was flushed with 10 mL per minute of nitrogen gas purge, during heating cycles. Elemental analyses were carried out by Galbraith Laboratories, Inc. of Knoxville, TN.

4-amino-1, 2, 4-triazole nitrate [$\text{C}_2\text{H}_5\text{N}_4^+$][NO_3^-]: Inside a nitrogen filled drybox, a Schlenk flask was charged with 0.9730 g, 11.6 mmoles, of 4-amino-1, 2, 4-triazole. Outside the drybox, dry methanol, 13 ml, was added through a disposable syringe along with a teflon stir bar under a brisk nitrogen flow. Concentrated nitric acid, 1.0702 g, 11.8 mmoles, was carefully added with a disposable glass pipet. The colorless, homogenous reaction mixture was stirred for one hour at ambient temperature. At the end of one hour, the stir bar was removed, and the solvent was evacuated off with a high vacuum overnight. The next day, the white crystalline product of 4-amino-1, 2, 4-triazole nitrate remained in very high yield, 1.6416 g, 11.6 mmoles, or 96.4% of theory. Excellent crystals could be formed from concentrated methanol solutions layered with diethyl ether. M.P. 69°C by DSC.

IR(cm^{-1}): 3350(mw), 3211(s), 3138(s), 3052(ms), 2979(m), 2912(m), 2833(mw), 1766(w), 1640(m), 1520(m), 1387(vs), 1328(ms), 1314(mw), 1201(mw), 1188(w), 1080(m), 1049(ms), 937(ms), 877(mw), 828(ms), 811(m), 678(mw), 656(mw), 625(s), 421(m).

Raman(cm^{-1}): 3236, 3186, 3145, 1646, 1565, 1550, 1425, 1395, 1348, 1326, 1285, 1273, 1177, 1080, 1038, 724, 709, 679, 659, 621, 415, 330, 315, 169, 124, 100, 84.

^1H NMR: (CD_3OD) +9.35 ppm (relative area 0.998); +5.32 ppm (relative area 1.512).

^{13}C NMR: (CD_3OD) +145.52 ppm singlet.

Elemental analysis: Theory. %C 16.33; %H, 3.43; %N, 47.61. Found. %C 16.00; %H, 3.50; %N, 47.49.

4-amino-1, 2, 4-triazole perchlorate [$\text{C}_2\text{H}_5\text{N}_4^+$][ClO_4^-]: Inside a nitrogen filled drybox, a Schlenk flask was charged with 1.1469 g, 13.6 mmol, of 4-amino-1, 2, 4-triazole. Dry methanol, 13 ml, was added through a disposable syringe along with a teflon stir bar under a brisk nitrogen flow. Concentrated perchloric acid, 1.9966 g, 13.9 mmol, was carefully added. The colorless, homogenous reaction mixture was stirred for one hour at ambient temperature. At the end of one hour, the stir bar was removed, and the solvent was evacuated off with a high vacuum overnight. The next day, the white crystalline product, 4-amino-1, 2, 4-triazole perchlorate remained in very high yield, 2.4693 g, 13.4 mmol, or 98.1% of theory. M.P. 84°C by DSC. Product could be recrystallized from MeOH/diethylether.

IR(cm^{-1}): 3355(m), 3303(mw), 3201(ms), 3153(ms), 3093(ms), 3042(m), 2970(mw), 2910(mw), 2827(w), 2023(w), 1742(mw), 1645(ms), 1518(ms), 1419(w), 1404(w), 1363(w), 1353(vw), 1327(m), 1215(mw), 1202(mw), 1154(ms), 1085(vs,vbr), 1050(s), 1030(s), 973(ms), 936(s), 877(m), 815(mw), 774(mw), 678(w), 661(w), 622(vs), 611(vs), 410(m).

Raman(cm^{-1}): 3350, 3287, 3251, 3156, 1630, 1560, 1523, 1418, 1330, 1222, 1158, 1130, 1106, 1078, 1033, 935, 912, 681, 632, 626, 612, 463, 457, 430, 104, 85.

^1H NMR: (CD_3OD) +9.309 ppm (relative area 1.022), +5.044 (relative area 1.721).

^{13}C NMR: (CD_3OD) +145.499 ppm singlet.

Elemental analysis: Theory. %C 13.01; %H, 2.73; %N, 30.36. Found. %C 12.48; %H, 2.78; %N, 29.73.

4-amino-1, 2, 4-triazole dinitramide $[C_2H_5N_4^+][N(NO_2)_2^-]$: Inside a drybox, one Schlenk flask was charged with 1.8782 g, 22.3 mmol of 4-amino-1, 2, 4-triazole, while another Schlenk flask was charged with 2.6453 g, 21.3 mmol of ammonium dinitramide. Subsequent manipulations of the reaction were carried out in total darkness, with only the assistance of a red light. The ammonium dinitramide was dissolved in methanol, 25 mL. The 4-amino-1, 2, 4-triazole was dissolved into 50 mL of methanol in a large round-bottomed flask. A column had been previously charged with a strong acidic cation exchange resin, which had been activated with 0.1M HCl solution, followed by water elution to remove excess acid, followed by a stepwise, solvent switchover to degassed, dry methanol. The ammonium dinitramide solution was eluted through the column (2 drops/second) into the stirred solution of 4-amino-1,2,4-triazole. Three separate aliquots, 100 mL each, of fresh methanol, were eluted through the ion exchange bed. After elution, the reaction mixture was vacuum stripped over a 36 hour period, until a constant mass was achieved, leaving a yellow oil in high yield, 4.0383 g, 20.6 mmol, 93% of theory. DSC revealed strong exotherm beginning around 150°C.

IR(cm^{-1}): 3330(s), 3230(s), 3138(s), 2700-3000(broad, strong), 1965(mw), 1752(mw), 1633(ms), 1522(vs), 1441(s), 1335(s), 1184(vs), 1076(ms), 1017(vs), 942(s), 877(ms), 824(ms), 758(s), 732(ms), 678(m), 660(m), 619(vs), 440(mw).

Raman(cm^{-1}): 3280, 3241, 3148, 1585, 1531, 1474, 1416, 1328, 1261, 1110, 1074, 1043, 989, 826, 777, 680, 481, 435, 410, 353, 300, 235, 85.

1H NMR: (CD_3OD) +9.34 ppm (relative area 1.000), +5.214 (relative area 1.811).

^{13}C NMR: (CD_3OD) +145.57 ppm singlet.

Elemental analysis not carried out due to the sensitivity of the material.

1, 2, 4-triazole nitrate $[C_2H_4N_3^+][NO_3^-]$: A flask was charged with 1.0458 g, 15.1 mmol, of 1, 2, 4-triazole, dissolved with methanol, 20 mL, and stirred vigorously. Concentrated nitric acid, 1.3925 g, 15.2 mmol, was carefully added, and the reaction mixture stirred for an additional 30 minutes, whereupon the stir bar was removed, and the

solvent was evacuated off. After 18 hours of evacuation, a white crystalline solid remained in nearly quantitative yield, 1.9910 g, 99.6% of theory. M. P. 137°C by DSC. IR(cm^{-1}): 3152(m), 3101(s), 3035(mw), 3008(w), 2919(m), 2791(m), 2725(m), 2642(m), 2643(m), 2509(w), 1800(w), 1574(m), 1527(w), 1481(mw), 1460(m), 1445(m), 1419(s), 1401(s), 1383(s), 1322(vs), 1278(mw), 1263(m), 1194(m), 1160(m), 1033(w), 978(mw), 944(s), 915(ms), 821(w), 732(w), 714(mw), 671(m), 634(ms). Raman(cm^{-1}): 3153, 3101, 3036, 2950-2650(br), 1530, 1463, 1428, 1395, 1348, 1283, 1274, 1265, 1193, 1168, 1129, 1049, 1032, 937, 731, 717, 660, 640, 182, 134, 86, 69. ^1H NMR: (CD_3OD) +9.287 ppm (relative area 1.000), +5.189 (relative area 0.997). ^{13}C NMR: (CD_3OD) +143.947 ppm singlet. Elemental analysis: Theory: %C 18.19; %H, 3.05; %N, 42.42. Found: %C 18.37; %H, 2.94; %N, 42.31.

1, 2, 4-triazole perchlorate $[\text{C}_2\text{H}_4\text{N}_3^+][\text{ClO}_4^-]$: A flask was charged with 1.3745 g, 19.9 mmoles, of 1, 2, 4 -triazole, dissolved in methanol, 15 ml, and stirred vigorously with a teflon stir bar. Concentrated perchloric acid, 2.8589 g, 19.9 mmoles, was carefully added and the reaction was stirred for an additional 30 minutes. The teflon stir bar was removed, and methanol was removed by evacuation overnight. Ethanol, 10 ml was added to the resultant solid, which, with warming, dissolved, which was subsequently layered with 25 ml of diethylether. After 24 hours a large crop of crystals had formed. The crystals were washed with 3 X 10 ml of dry ether and vacuum dried, for a yield of 1.8579 g of product. The mother solution was layered with an additional 40 ml of diethyl ether yielding an additional 1.2863 g of product, for a total yield of 3.1442 g, 93% of theory. M. P. 89°C by DSC.

IR(cm^{-1}): 3150(m), 3132(s), 3070(m,br), 3006(ms), 2946(ms), 2917(ms), 2879(s), 2810(s), 2782(m), 2755(mw), 1645(w), 1557(ms), 1517(mw), 1414(ms), 1379(s), 1273(w), 1258(w), 1162(s), 1148(s), 1112(vs), 1091(vs), 1030(ms), 958(w), 937(m), 882(w), 815(ms), 657(mw), 636(m), 626(ms), 615(s). Raman(cm^{-1}): 3300, 3150, 1540, 1414, 1392, 1267, 1182, 1170, 1101, 1040, 956, 938, 930, 913, 662, 636, 631, 621, 465, 458, 453, 137, 84. ^1H NMR: (CD_3OD) +9.349 ppm (relative area 1.000), +5.107 (relative area 1.000).

^{13}C NMR: (CD_3OD) +143.374 ppm singlet.

Elemental analysis: Theory: %C 14.17; %H, 2.38; %N, 24.79. Found: %C 14.45; %H, 2.28; %N, 24.61.

1, 2, 4-triazole dinitramide $[\text{C}_2\text{H}_4\text{N}_3^+][\text{N}(\text{NO}_2)_2^-]$: Inside a drybox, one Schlenk flask was charged with 0.6801 g, 9.8 mmol of 1, 2, 4-triazole, while another Schlenk flask was charged with 1.2103 g, 9.8 mmol of ammonium dinitramide. Outside the drybox, dry methanol, 20 ml for each, was added to both the 1, 2, 4-triazole and the $[\text{NH}_4][\text{N}(\text{NO}_2)_2]$, completely dissolving both. The 1, 2, 4-triazole solution was transferred to a 1000 mL flask, and stirred vigorously with a large teflon stir bar. The ammonium dinitramide solution was added to the top of the ion exchange column with 30ml of fresh methanol. The ammonium dinitramide solution was eluted at 2 drops/second into the vigorously stirred triazole solution. Three aliquots of fresh methanol (100 ml) were used to effect complete elution of the dinitramide solution through the column. At the end of the elution, the methanol was rotovapped away from the reaction solution, leaving a viscous, straw colored oil. The oil was transferred to a preweighed Schlenk flask, and further evacuated. The oil was then dissolved in 10 ml of ethyl acetate and layered carefully with 20 ml of dry, diethyl ether and stored at 4°C for 48 hours. A large crop of crystals was recovered which was washed with fresh ether and was vacuum dried resulting in a yield of 1.6035 g, 93% of theory. M. P. 75°C by DSC.

IR(cm^{-1}): 3303(ms, br), 3158(s), 3140(s), 3098(m), 3050(mw), 2914(ms), 2812(ms), 2612(mw, br), 1685(w), 1566(ms), 1542(vs), 1520(vs), 1418(s), 1399(s), 1337(mw), 1271(mw), 1235(mw), 1204(vs), 1178(vs), 1158(vs), 1110(mw), 1033(ms), 1025(ms), 980(w), 943(ms), 917(mw), 708(mw), 851(w), 825(m), 760(m), 745(w), 733(w), 720(m), 664(mw), 633(m).

Raman(cm^{-1}): 3300, 3160, 3130, 3041, 1534, 1435, 1397, 1335, 1268, 1215, 1184, 1135, 1115, 1049, 1036, 1018, 1012, 962, 827, 759, 750, 648, 620, 493, 481, 309, 149, 104, 81.

^1H NMR: (CD_3OD) +9.349 ppm (relative area 1.000), +5.736 (relative area 0.962).

^{13}C NMR: (CD_3OD) +143.360 ppm singlet.

Elemental analysis: Theory: %C 13.64; %H, 2.29; %N, 47.73. Found: %C 13.96; %H, 2.15; %N, 47.17.

1, 2, 3-triazole nitrate $[C_2H_4N_3^+][NO_3^-]$: Inside a drybox, a flask was charged with 0.5726 g.; 8.3 mmols, of 1, 2, 3-triazole. Methanol, 20 ml, was added by a disposable syringe along with a teflon stir bar, resulting in the complete dissolution of the heterocycle. Concentrated nitric acid, 0.7754 g, 8.5 mmols, was added carefully to the stirred solution. The mixture was allowed to stir for an additional 30 minutes, whereupon the stir bar was removed, and the solvent was evacuated off with a high vacuum overnight. The resultant white solid was dissolved in 5 ml of dry ethanol, with gentle heating, and then was layered with 30 ml of dry, diethyl ether, and left overnight, resulting in a large crop of needles. Yield 1.0829 g, 98.8% of theory. M. P. 68°C by DSC.

IR(cm^{-1}): 3160(s), 3133(s), 2980(mw), 2924(m), 2850-2450(med, br), 1955w0, 1883(w), 1588(m), 1540(w), 1509(mw), 1454(m), 1408(vs), 1390(vs), 1316(vs), 1271(s), 1183(w), 1153(w), 1091(m), 1045(mw), 999(w), 953(mw), 928(m), 825(m), 723(mw), 714(mw).

Raman(cm^{-1}): 3160, 3136, 3041, 2903, 1604, 1586, 1503, 1486, 1406, 1384, 1280, 1180, 1152, 1094, 1045, 942, 929, 724, 715, 641, 176, 116, 84, 72.

1H NMR: (CD_3OD) +8.386 ppm (relative area 1.000), +5.789 (relative area 0.926).

^{13}C NMR: (CD_3OD) +129.55 ppm singlet.

Elemental analysis: Theory. %C 18.19; %H, 3.05; %N, 42.42. Found: %C 19.25; %H, 3.06; %N, 41.44

1, 2, 3-triazole perchlorate $[C_2H_4N_3^+][ClO_4^-]$: Inside a drybox, a flask was charged with 0.6162 g, 8.9 mmols, of 1, 2, 3-triazole. Ethanol, 7 ml, was added by a disposable syringe under vigorous nitrogen purge, along with a teflon stir bar, resulting in the complete dissolution of the heterocycle. Concentrated perchloric acid, 1.2834 g, 8.9 mmols, was added carefully to the resultant solution. After reaction was stirred for 30 minutes at ambient temperature, teflon stir bar was removed, and ethanol was removed by evacuation overnight. The resultant white solid was dissolved in 7 ml of warm isopropyl alcohol, and layered with 60 ml of diethyl ether. A large crop of white plates

were isolated 48 hours later, which were washed with fresh ether, and vacuum dried.

Yield, 1.2845 g, 85% of theory. M. P. 73°C by DSC.

IR(cm^{-1}): 3145(m), 3120(ms), 3108(ms), 3016(m), 2923(ms), 2883(ms), 2827(ms), 2791(ms), 2730(ms), 2674(ms), 1777(w), 1541(ms), 1465(w), 1417(w), 1357(mw), 1348(mw), 1280(mw), 1273(mw), 1148(s), 1130(mw), 1117(mw), 1107(s), 1086(vs), 968(mw), 950(m), 940(mw), 902(mw), 809(ms), 638(ms), 626(ms).

Raman(cm^{-1}): 3160, 3136, 3041, 2903, 1604, 1586, 1503, 1486, 1406, 1384, 1280, 1180, 1152, 1094, 1045, 942, 929, 724, 715, 641, 176, 116, 84, 72.

^1H NMR: (CD_3OD) +8.588 ppm (relative area 0.998), +5.338 (relative area 0.890).

^{13}C NMR: (CD_3OD) +129.06 ppm singlet.

Elemental analysis: Theory: %C 14.17; %H, 2.38; %N, 24.79. Found: %C 14.17; %H, 2.48; %N, 24.81.

1, 2, 3-triazole dinitramide [$\text{C}_2\text{H}_4\text{N}_3^+$][$\text{N}(\text{NO}_2)_2^-$]: Inside a drybox, one Schlenk flask was charged with 0.5473 g, 7.9 mmol of 1, 2, 3-triazole, while another Schlenk flask was charged with 0.9811 g, 7.9 mmol of ammonium dinitramide. Methanol, 20 ml, was added to each reagent, totally dissolving both. The 1, 2, 3-triazole solution was transferred to a 1000 ml flask, with 3 X 20 ml aliquots of fresh methanol, and a large teflon stir bar was added. The ammonium dinitramide solution was added to the top of the ion exchange column with 3 X 10 ml of fresh methanol. The ammonium dinitramide solution was eluted at 2 drops/second into the vigorously stirred triazole solution. Three aliquots of fresh methanol (100 ml) were used to effect complete elution of the dinitramide through the column. The methanol was rotovapped away from the reaction solution leaving a viscous, straw colored oil. The oil was transferred to a preweighed Schlenk flask, and further evacuated for 16 hours more. The resultant white mass, 1.3812 g, 99% of theory, was dissolved in 10 ml of ethyl acetate and layered with 40 ml of diethyl ether and stored at 4°C. After 24 hours, a large crop of white crystals were recovered, yield 1.2078 g, 87% of theory. M. P. 61°C by DSC.

IR(cm^{-1}): 3158(m), 3124(m), 3103(ms), 3001(mw), 2930(ms), 2822- 2620(m, br), 2002(w), 1783(w), 1578(mw), 1550(s), 1542(vs), 1525(m), 1450(m), 1357(w), 1347(w), 1322(mw), 1281(w), 1273(w), 1189(vs), 1170(vs), 1127(mw), 1086(ms), 1070(w),

1033(s), 1025(s), 962(ms), 952(m), 927(mw), 871(m), 789(m), 760(w), 448(m), 441(mw).

Raman(cm^{-1}): 3160, 3149, 3081, 1525, 1440, 1419, 1323, 1286, 1186, 1125, 1080, 1011, 943, 828, 760, 752, 495, 450, 317, 123, 85.

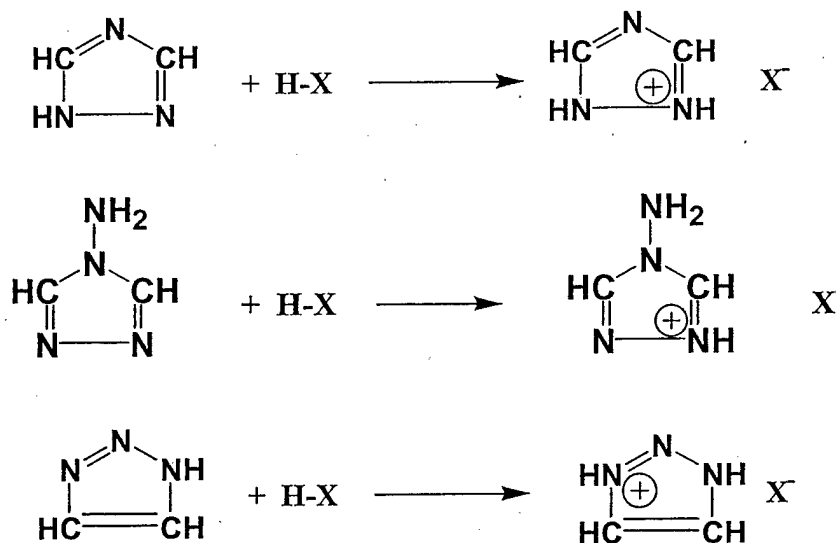
^1H NMR: (CD_3OD) +8.595 ppm (relative area 1.000), +5.553 (relative area 1.014).

^{13}C NMR: (CD_3OD) +128.92 ppm singlet.

Elemental analysis: Theory: %C 13.64; %H, 2.29; %N, 47.73. Found: %C 12.91; %H, 2.28; %N, 46.55.

DISCUSSION.

The starting heterocycles, 1-H-1, 2,4-triazole, 4-amino-1, 2, 4-triazole, and 1-H-1,2,3-triazole were readily soluble in dry methanol, and subsequent reactions were carried out in this media, with the desired form of the strong acid.(Figure 2)



Where H-X is HNO_3 , HClO_4 , or " $\text{HN}(\text{NO}_2)_2$ " and X^- is NO_3^- , ClO_4^- , or $\text{N}(\text{NO}_2)_2^-$.

Figure 2. Reactions of the triazole systems with strong acids to form salts.

For the synthesis of the nitrate and perchlorate salts, the concentrated, aqueous solutions of both acids were used, while for the synthesis of the dinitramide salts, since free dinitramine is known to be explosive^{5,6}, the use of a strongly acidic, cation exchange

resin bed was employed. All of the salts were formed in nearly quantitative yield and high purity, and could be recrystallized from concentrated alcoholic solutions layered with diethyl ether. With the 1,2,4-triazole systems, the product salts had lower melting points than the parent heterocycles, except for 1,2,4-triazolium nitrate and were well below 100°C. These new materials should be classified as new, highly energetic members belonging to the well known class of ionic liquids⁷⁻¹⁰.

The two ring systems used have significantly different base properties. The pK_a usually gives a good reference to how easily a material can be protonated. 4-amino-1, 2, 4-triazole has a pK_a of 2.25¹¹, 1, 2, 4-triazole has a pK_a of 10.04^{12,13}, while 1-H-1,2,3-triazole has a pK_a of 8.2¹¹. Several orders of magnitude in base strength is rather surprising, when the only difference is the presence of one N-amino group. NH_2 groups are usually thought of as proton base sites in many molecules. However, in high nitrogen heterocycles, almost the opposite is true with the amino group acting as an electronegative, electron withdrawing group. Other authors have looked at theoretical calculations of possible conformations of the pendant NH_2 group, and the interactions of the pendant amino nitrogen's lone pair with the aromatic-like structure of several high-nitrogen heterocyclic rings.¹⁴ These electronic interactions between the pendant amino group and the ring significantly reduce the basicity of the lone pair on the pendant $-NH_2$ group. In the studies carried out here, there was a marked difference in the pH of the product salts. With the 4-amino-1, 2, 4-triazole salts, the pH of the product solutions were around 2, while for the 1, 2, 4-triazole and 1,2,3-triazole salts the pH was measured to be around 4-5.

Vibrational spectroscopy was useful in qualitative analyses of all of the salts. Most obvious in all spectra, were the bands of the respective energetic anions. These bands usually have characteristic "fingerprints", which are easily identified in both pattern and in frequency. The anion bands of nitrate, perchlorate, and dinitramide are well known in both the infrared and the Raman spectra. Most of the anion bands, which were found in the new salts, matched well with the known frequency values for the anions in other well-studied cation-anion systems. The nitrate anion, NO_3^- , usually has a strong stretch at 1345 cm^{-1} in the infrared and a strong band around $1043\text{-}1050\text{ cm}^{-1}$ in the Raman spectrum.^{15,16} The perchlorate anion, ClO_4^- , has a strong broad stretch centered

around 1119 cm^{-1} in the infrared spectra, and strong bands at 958 cm^{-1} and 459 cm^{-1} in the Raman spectrum.^{17, 18} The dinitramide anion, $\text{N}(\text{NO}_2)_2^-$, has strong stretches in the infrared spectrum at around 1530 cm^{-1} , 1445 cm^{-1} , 1345 cm^{-1} , 1183 cm^{-1} , and 1025 cm^{-1} , and strong bands in the Raman at 1335 cm^{-1} and 830 cm^{-1} .¹⁹⁻²² Other tendencies, which were apparent in the infrared and Raman spectra, were the shifts of the N-H. It has been noted that in many amine and hydrazine systems, that upon protonation of a terminal amine functional group, $-\text{NH}_2$ to $-\text{NH}_3^+$, that there is drop in the N-H stretching frequencies, with a corresponding increase in adjacent C-H stretching frequencies.²³⁻²⁵ There is also the appearance of a large broad band ranging from 2400 cm^{-1} to 3000 cm^{-1} due to $\text{R}_3\text{N}^+-\text{H}\cdots\text{X}^-$ hydrogen bonding interactions, which has been observed in other protonated nitrogen systems.²⁶⁻²⁸ In heterocyclic systems, however, protonation usually occurs on of the heterocyclic ring nitrogen atoms, either atom N(1) or N(2) of the 1, 2, 4-heterocyclic ring. When this occurs, there is an increase in the NH_2 - stretching frequencies, rather than a drop. This has been noted by previously with 1, 2, 4-triazole and 4-amino-1, 2, 4-triazole systems.⁴ In the related triazole ring systems, 3-amino-1, 2, 4-triazole, and 3,5-diamino-1, 2, 4-triazole, proton attachment has been observed on the heterocyclic ring rather than the pendant NH_2 groups.²⁹⁻³²

In all of the salts, which were studied here, there was an increase from 20 cm^{-1} to 40 cm^{-1} in the NH_2 asymmetric stretching area ($3200\text{ cm}^{-1} - 3400\text{ cm}^{-1}$), with the simultaneous appearance of the broad band from 2400 cm^{-1} to 3000 cm^{-1} , which is indicative of a protonated nitrogen atom. This evidence points to the fact that a nitrogen atom in the ring structure, which previously had no N-H linkage, was protonated, which leads to the observed N-H stretches at lower frequencies. Unfortunately, assigning C-H stretches with any confidence was almost impossible with the appearance of the large band of N-H stretches, in order to see if there was the corresponding increase in the adjacent C-H stretching frequencies.

Proton nmr produced strong evidence for the existence of the protonated heterocycles. In all cases, there was a downfield shift of the C-H resonances in the ^1H nmr, indicative of deshielding of the hydrogen atoms attached to the carbon atoms. This effect comes from the loss of electron density in the heterocyclic ring, due to the protonation of one of the adjacent, bonded nitrogen atoms. The resonances due to the N-

H bound protons were all one peak, which had also shifted downfield from the starting heterocycles.^{11, 33-35} In the ¹³C nmr, with the "loss" of some of the electron density of the heterocyclic ring, there was a slight upfield shift of the ¹³C resonance. These effects have been observed in several other nitrogen heterocyclic systems upon protonation by strong acids.^{11, 14} Hence, the ¹H and ¹³C spectra strongly supported the existence of protonated heterocyclic species in solution.

Density is an important physical property of any new energetic material. The densities of all of the new salts, except 4-amino-1,2,4-triazolium dinitramide, were measured by helium displacement methods and are in Table 1 along with the calculated densities³⁶⁻³⁹, with one important exception. We have found that in the case of monoprotonated nitrogen base systems, more reasonable densities are often obtained without using the 0.232 angstroms³ value for the formal N⁺, but rather the values for the expected nitrogen atom environment. Several of the materials have relatively high densities for simple mono protonated salts with two of the perchlorate salts being well over 1.8 g/cm³.

<u>Energetic Salt</u>	<u>Calculated density</u>	<u>Observed density</u>
4-amino-1, 2, 4-triazole nitrate	1.58 g/cm ³	1.60 g/cm ³
4-amino-1, 2, 4-triazole perchlorate	1.78 g/cm ³	1.81 g/cm ³
4-amino-1, 2, 4-triazole dinitramide	1.66 g/cm ³	NT
1, 2, 4-triazole nitrate	1.55 g/cm ³	1.64 g/cm ³
1, 2, 4-triazole perchlorate	1.75 g/cm ³	1.85 g/cm ³
1, 2, 4-triazole dinitramide	1.64 g/cm ³	1.66 g/cm ³
1, 2, 3-triazole nitrate	1.55 g/cm ³	1.57 g/cm ³
1, 2, 3-triazole perchlorate	1.75 g/cm ³	1.79 g/cm ³
1, 2, 3-triazole dinitramide	1.64 g/cm ³	1.66 g/cm ³

Table 1. The calculated and observed densities of the simple heterocycle salts.

THERMAL AND INITIAL SAFETY STUDIES

In Table 1, the DSC melt, decomposition onset temperatures, as well as mass loss at 75°C per day of all the new salts are reported. Despite the low melting point of several of the salts, many have impressive liquid ranges before they begin to decompose, and

have excellent thermal stability at 75°C, which could be very useful in energetic materials. For thermal stability studies all of the new salts were put through TGA analysis. In this test, a small amount (20-40 mg) of new material is placed inside a small, pre-weighed quartz bucket, and carefully placed on a balance beam, inside a vertical, self made thermogravimetric analyzer (TGA). The sample cell containing the quartz bucket was flushed with ultrapure nitrogen gas for 1 hour, and then was heated isothermally at 75°C for 2-3 days. The drop in sample weight was monitored as a function of time. After an induction period, a few hours, the drop in sample weight was almost linear. This rate of weight loss was assumed to be due to sample decomposition. Using simple regression analysis, the linear decomposition rate, n , was calculated and is reported in Table 1.

Impact testing was carried out on an Olin-Mathieson style drop weight tester. A small amount of preweighed sample usually around 20 milligrams was placed in a brass cup for each test. A standard of HMX, 6 micron size, was tested previously as a standard, which gave a value of 34 kg-cm for five consecutive negative results. Drop heights were measured in centimeters with a falling 2 kg mass, and a minimum drop height is considered for five consecutive drops at a specific height and mass, with no change in the sample. From Table 2, it is obvious that there is a wide range in impact sensitivities from insensitive for both nitrate salts to the highly sensitive 4-amino-1,2,4-triazolium dinitramide and 1,2,3-triazolium perchlorate.

<u>Energetic Salt</u>	<u>Melting point</u>	<u>Decomposition onset</u>	<u>Mass loss @ 75 C</u>	<u>Impact (Kgcm)</u>
4-amino-1, 2, 4-triazole nitrate	69°C	180°C	0.58%	>200
4-amino-1, 2, 4-triazole perchlorate	84°C	210°C	0.02%	30
4-amino-1, 2, 4-triazole dinitramide	20°C	146°C	0.29%	<5
1, 2, 4-triazole nitrate	137°C	182°C	0.88%	>200
1, 2, 4-triazole perchlorate	89°C	285°C	0.03%	114
1, 2, 4-triazole dinitramide	75°C	120°C	1.62%	98
1, 2, 3-triazole nitrate	110°C	125°C	73.5%	>200
1, 2, 3-triazole perchlorate	73°C	200°C	0.05	<5
1, 2, 3-triazole dinitramide	61°C	80°C	NT	NT

Table 2. Physical properties and initial safety testing data for the new triazolium salts.

These two highly energetic salts should be handled with extreme care. However, most of the salts are less sensitive to impact than the highly used HMX.

CONCLUSIONS

4-amino-1,2,4-triazole, 1-H-1,2,4-triazole, and 1-H-1,2,3-triazole react with acid forms of well known oxidizing anions including nitrate, perchlorate, and dinitramide, to form highly energetic, low melting salts. These materials are made in one step, high yield and purity reactions, and most exhibit excellent physical properties including long liquid ranges after the melt, and should be considered new members of the growing and well documented class of ionic liquids. These highly energetic salts have good thermal stabilities at elevated temperatures, and most have reasonable impact values, and some should find practical uses.

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